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Catalytic ceramic papers for diesel soot oxidation: a spray method for enhanced performance

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Abstract

A spray method is proposed to improve the catalytic properties of ceramic papers to be used as catalytic filters for removing diesel soot particles. Small particles of Ce and Co oxides, acting as active centers for the combustion of the soot retained by the filter, are efficiently and homogeneously deposited. On the contrary, the application of the conventional drip method results in bigger particles mainly agglomerated at the crossings between the fibers of the ceramic paper. As a result, catalytic papers prepared by the spray method exhibit much higher performance with soot combustion temperatures decreased by ~30°C.

Keywords

Diesel soot combustion, spray drying, catalytic ceramic paper, exhaust catalyst, cerium, cobalt

1. Introduction

The most adequate technology for the abatement of soot particles coming from diesel engines is the one that employs catalytic filters [1-4]. Nowadays, commercialized filters consist of SiC monoliths with active elements on it [5-8]. As an alternative, it was proposed to use ceramic papers as suitable materials to conform flexible structured catalysts for diesel filters [9-14]. Indeed, such papers are flexible, easy to handle and present suitable mechanical properties to resist assays from a test bench in which they were placed inside a metal housing, at the exhaust pipe outlet of a Corsa 1.7 diesel vehicle [9]. Optimal mechanical properties were obtained through the incorporation of a suspension of CeO_2 nanoparticles (10 or 20 wt. % CeO_2) during the papermaking process.

The passive regeneration of the filter implies the addition of catalytic components [15]. In this contribution, two different methods are used and compared in order to achieve the best distribution of the catalytic components (cerium and cobalt oxides) throughout the ceramic matrix: drip impregnation and spray deposition. The first method involves the impregnation by dripping a solution of precursor salts containing the desired catalytic components, followed by calcination. The second one is inspired by the aerosol process [16, 17], which is currently emerging as a powerful tool for the preparation of advanced materials, especially catalysts [18-22]. The preparation is carried out in a dedicated experimental setup (Figure 1), which consists of an aerosol generating system coupled with a tubular oven in which the formed droplets are dried rapidly. This dried aerosol is directly sprayed onto the ceramic paper disc.

The catalytic behavior was studied by means of TPO experiments in order to evaluate the feasibility of passive regeneration of the filters and physicochemical properties were evaluated by XRD and SEM.

2. Experimental

2.1. Ceramic paper preparation

The preparation method of the ceramic paper was based on a procedure similar to that used in the production of conventional paper from cellulose fibers and that is in detailed described elsewhere [9]. The ceramic fibers, 660 μm long (SiO_2-Al_2O_3) were dispersed in the aqueous medium in which a binder was added (10-20 wt.% of CeO_2 nanoparticles, Nyacol). Ribbon–shaped cellulose fibers, 3000 μm long, were also incorporated to enhance the retention of the ceramic fibers during the formation stage. The cationic polymer used was polyvinylamine (PVAm) (Luredur PR 8095) and the anionic polymer was anionic polyacrylamide (A-PAM).

A two-step method was employed for the preparation of catalytic ceramic papers. In the first step, following the papermaking technique, a sheet (16.5 cm in diameter) was formed and dried under controlled atmosphere (23 °C, 50% R.H.) for 24 h and finally calcined in air at 600 °C for 2 h. The second step corresponded to the deposition of the catalytic ingredients. Two series of catalysts were prepared, one following the conventional dripping method and the other using the spray technique.

2.2. Drip impregnation

The incorporation of the catalytic ingredients by drip impregnation was carried out using an equimolecular solution of $Ce(NO_3)_3$ and $Co(NO_3)_2$, which was prepared by dissolving the necessary amount of each precursor salt in the volume of water calculated to saturate the paper structure, so as to load 4 wt.% of $Ce(NO_3)_3$+$Co(NO_3)_2$. The impregnated ceramic papers were then dried at room temperature overnight and calcined in a furnace at 600 °C for 2 h. The catalysts were denoted as 10Ce-Ce-Co-600-Imp and 20Ce-Ce-Co-600-

Imp, where “10Ce” or “20Ce” indicate the wt.% CeO_2 binder used, “Ce-Co” the active components added, “600” the final calcination temperature and “Imp”, the use of the drip impregnation method.

2.3. Spray deposition

In the second case , a mixed equimolecular solution of $Ce(NO_3)_3$ (0.622 g/l) and $Co(NO_3)_2$ (0.556 g/l) was placed in an atomizer (6-Jet 9306A atomizer from TSI) and sprayed with an air pressure of 30 psi (Fig. 1). The aerosol was dried by passing through a tubular furnace heated at 400°C and the particles were directly sprayed onto the ceramic papers. Any excess particles exiting across the paper were retained by an absolute filter. The spraying time (6-8 h) were adjusted in order to load 4 wt.% $Ce(NO_3)_3$+$Co(NO_3)_2$ on the ceramic paper discs. The sprayed ceramic papers were then calcined in a furnace at 600 °C for 2 h. The actual loading was verified by weighing. Catalytic papers are denoted as 10Ce-Ce-Co-600-Spray and 20Ce-Ce-Co-600-Spray.

2.4. Characterization

Crystalline phases were determined with a Shimadzu XD-D1instrument with monochromator using CuKα radiation at a scan rate of 2 °/min, from 2θ = 15 ° to 80 °. The pieces of about 16 mm in diameter were supported in a special sample holder designed for the XRD analysis. The software package of the equipment was used for the phase identification from the X-ray diffractograms.

A SEM Jeol JSM-35C equipment was employed, operated at 20 kV acceleration voltage. Samples were glued to the sample holder with Ag painting and then coated with a thin layer of Au in order to improve the images.

2.5. Soot combustion

Soot particles were produced by burning a commercial diesel fuel (YPF, Argentina) in a glass vessel. After being collected from the vessel walls, the soot was dried in a stove at 120 °C for 24 h. Soot particles were dispersed in n-hexane using an ultrasonic bath in order to obtain a homogeneous suspension of 600 ppm of diesel soot in n-hexane. The incorporation of soot particles to the ceramic paper pieces (2 cm in diameter discs) was carried out by adding the suspension drop wise until saturation, and then drying at room temperature.

The catalytic activity of the ceramic papers for the soot combustion was studied by Temperature Programmed Oxidation (TPO). For this purpose, the structured samples + soot were heated at 5 °C/min from room temperature up to 600 °C in O_2 (18%)+NO (0.1%) diluted in He (total flow 20 ml/min) in a flow equipment designed for this purpose. We have chosen the oxygen concentration (18%) in order to compare our catalytic results with others previously published. The exhaust gases were analyzed with a Shimadzu GC-2014 chromatograph (with TCD detector).

In order to assess catalysts stability, two different experiments were carried out: 1) Thermal ageing in air at 900°C during two hours, and 2) several consecutive TPO cycles. In the latter, catalytic ceramic paper discs were recovered at the end of each TPO run and re-impregnated with soot before being tested again in TPO (room temperature to 700°C).

3. Result and discussion

SEM micrographs of the catalytic ceramic papers prepared using both preparation methods are shown in Figure 2. Open structures are observed both for 10Ce-Ce-Co-600-Imp

and 10Ce-Ce-Co-600-Spray. In order to analyze the penetration of Co and Ce introduced by drip impregnation and spray deposition methods through the thickness of the ceramic paper, SEM micrographs were obtained both on the top face (Figs. 2A and C) and also on a slice obtained by cutting the disc at the middle of its thickness (Figs. 2B and D). For both impregnation methods the amount of particles deposited both on the top face and in the bulk appear similar. It is interesting to note that catalytic particles formed in the spray process are retained inside the paper that is acting as a filter, which is the behaviour expected during the operation in the tail pipe of a diesel exhaust.

In the case of the drip impregnation method Ce and Co oxides mainly appear concentrated in the form large chunks (> 10 μm, see Table 1) on ceramic fibers crossings. On the contrary, when the spray method is employed (10Ce-Ce-Co-600 Spray), smaller catalytic particles (at least one order of magnitude smaller, see Table 1) appear well distributed throughout the ceramic matrix (Fig. 2C and D).

A closer view of the catalytic ceramic papers deposited by drip impregnation (Figures 3A and B) shows agglomerates of catalytic particles larger than 5 μm and also bare ceramic fibers both on the top face and in the bulk, revealing a non-homogeneous distribution of the catalytic components. Most probably, capillary forces exerted during the drying step trigger the accumulation of the active elements at the fibers crossings. On the contrary, when using the spray deposition method (Fig. 3C and D) smaller agglomerates are formed (<1 μm), more uniform, homogeneous and better distributed along the thickness of the matrix. Therefore, the spray technique can be considered more adequate to deposit active species on ceramic papers in order to develop catalytic ceramic filters for diesel exhaust post-treatment.

Only CeO_2 diffraction peaks both for impregnated and sprayed samples were observed by XRD (Figure 4), which might indicate that Co_3O_4 crystallites are smaller than 4 nm. No significant differences were observed for structured catalysts prepared using 10 or 20 wt.% CeO_2. Nevertheless, as the amount of CeO_2 nanoparticles increased, a higher number of bigger CeO_2 patches was formed [9]. The Scherrer equation was used to calculate CeO_2 crystallite sizes (Table 1). Crystallite sizes were similar for both preparation methods employed and for different amounts of CeO_2 used as binder (~7 nm).

TPO profiles (Figure 5) clearly evidence that the spray method produced more active catalysts, as curves corresponding to sprayed samples appear left-shifted by as much as 30°C, resulting in a peak of combustion at about 450°C. This is in the same range as previously reported systems of similar composition [23-25]. No difference was found between catalytic activities of ceramic papers prepared using either 10 or 20 wt.% CeO_2. According to SEM and XRD, the spray method allowed the formation of smaller catalytic particles better dispersed throughout the support. This in turns is proposed to improve the contact between soot and catalyst particles, thereby increasing significantly the catalytic activity.

On the other hand, stability, it is a matter of concern in soot combustion catalysts [26, 27]. For example, Banus et al. studied the stability of Co-Ba-K/ZrO_2 coated onto metallic foam and on Al_2O_3 foam [28, 29] and concluded that severe ageing temperatures lead to sintering and loss of soot oxidation ability. In a previous work [9] we also addressed this issue for Co and Ce impregnated ceramic papers containing higher cobalt loadings. The catalyst suffered deactivation after a severe treatment at 900°C in air during two hours. This deactivation was attributed to reactions between the active components and the material of the fibers, forming silicates and/or aluminates. Thus, here the same ageing treatment was performed with the catalyst prepared using the spray method (10-Ce-Ce-Co-S900). A similar

activity loss was observed (Figure 5). Recycling experiments were also done by carrying several cycles of reaction, after which we also observed deactivation (see supplementary information). Further work is thus needed to address this issue of stability by developing specific strategies that prevent sintering, attrition and active species detaching. In this vein, Fornasiero et al. [30] studied the catalytic stability of functionalized Fe-Cr-Al alloy fibers, where the ageing treatment in static air at 800 °C led to an appreciable catalytic deactivation. To address this issue and enhance the adhesion of the washcoat, they proposed metallic stack, made by a network of thin metallic wires functionalized by the deposition of nanocomposite heterogeneous catalysts. In ceria-based soot combustion catalysts, sintering can be effectively suppressed for example by the formation of solid solutions, as reviewed recently by Liu et al. [23].

Conclusions

The spray method provides of an efficient way to homogeneously deposit Co and Ce oxide in the form of small particles highly dispersed on the fibers of ceramic papers prepared by the papermaking method. These particles can act as active centers for the combustion of the soot retained when the catalytic paper is used as a diesel soot filter. On the contrary, the application of the conventional drip method results in bigger particles mainly agglomerated as bulky chunks at the crossings between the fibers of the ceramic paper. Thus, the spray method improved the contact between soot and catalyst particles, increasing the catalytic activity as shown by TPO experiments (significant improvement of 30 K). It is important to emphasize that for the manufacture of these catalytic filters very low catalyst loadings have been used, obtaining excellent temperatures of maximum soot combustion rate, which makes it an economical and easily scalable method.

However, the catalytic filter made of fibers with active phases deposited by the spray method suffers deactivation either when treated at high temperature or after reaction cycles. Deactivation probably occurs due to reaction between cobalt and the fibers at high temperature and/or to active component detaching. Future work will be needed to improve the stability of the catalysts either by changing the material of the fibers or subjecting them to a chemical passivation, so that they can be practically applicable under stringent conditions.

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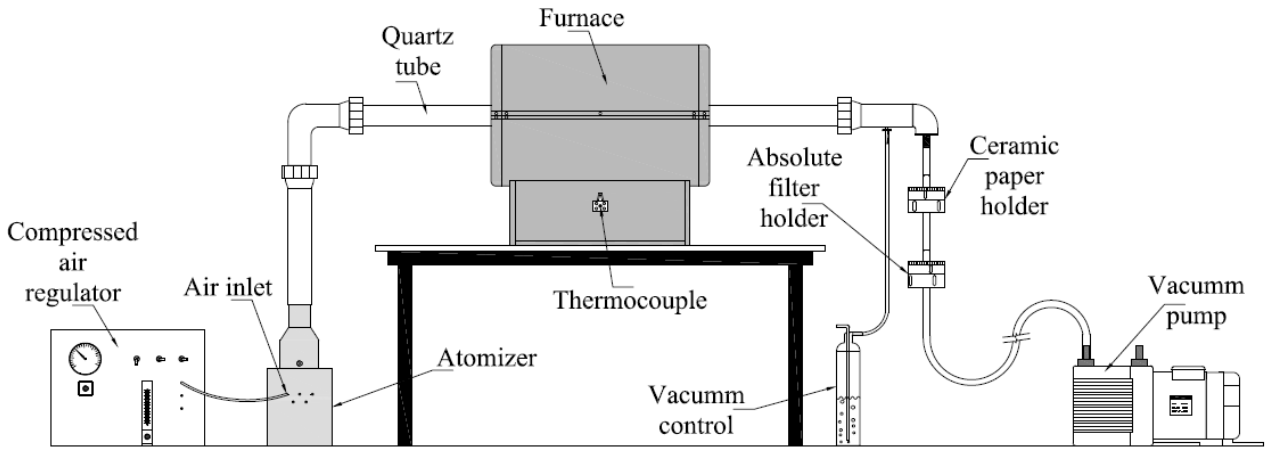


Figure 1. Scheme of the spray deposition setup.

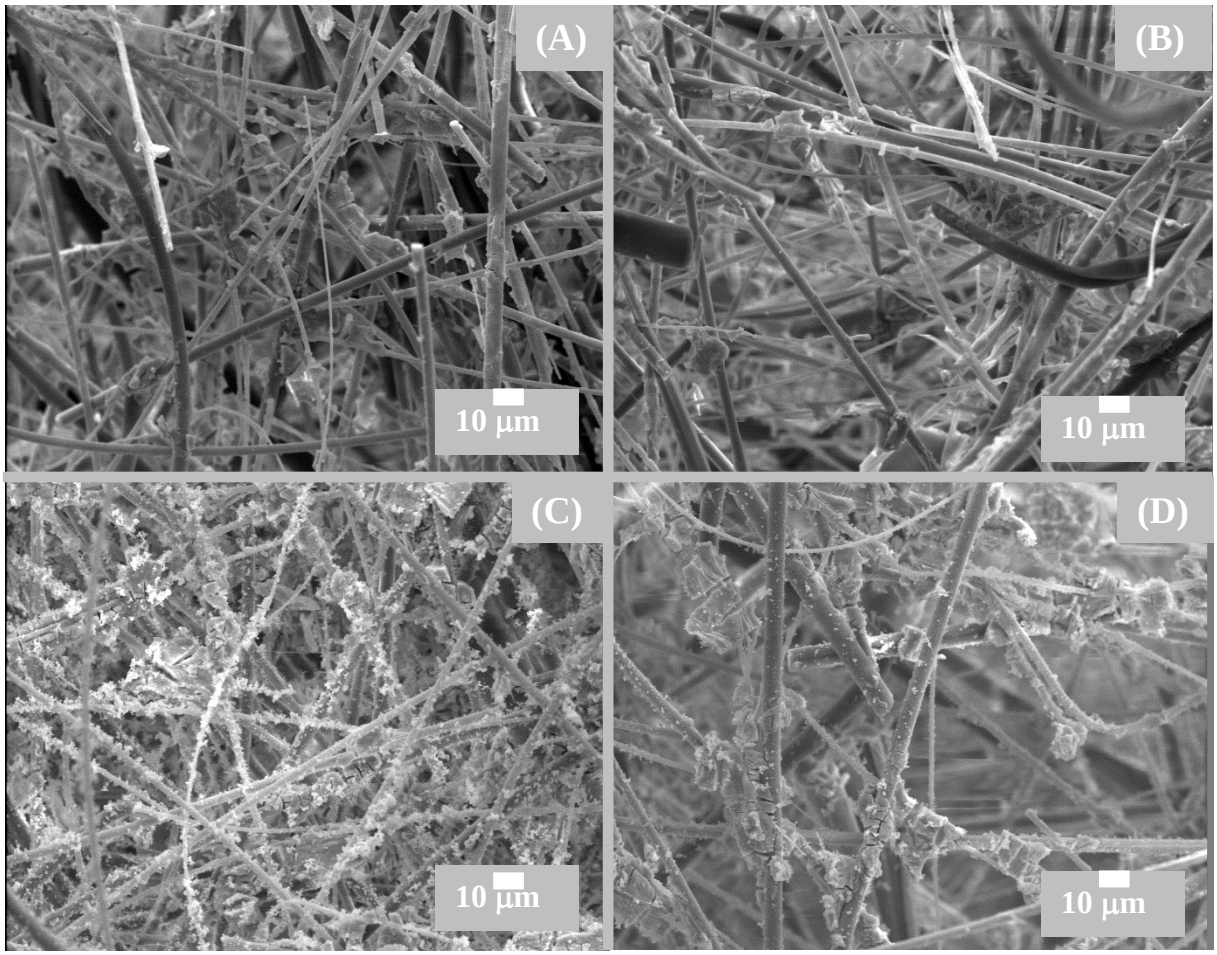


Figure 2. SEM micrographs. (A) Top face: 10Ce-Ce-Co-600 Imp. (B) Bulk: 10Ce-Ce-Co-600 Imp. (C) Top face: 10Ce-Ce-Co-600 Spray. (D) Bulk: 10Ce-Ce-Co-600 Spray.

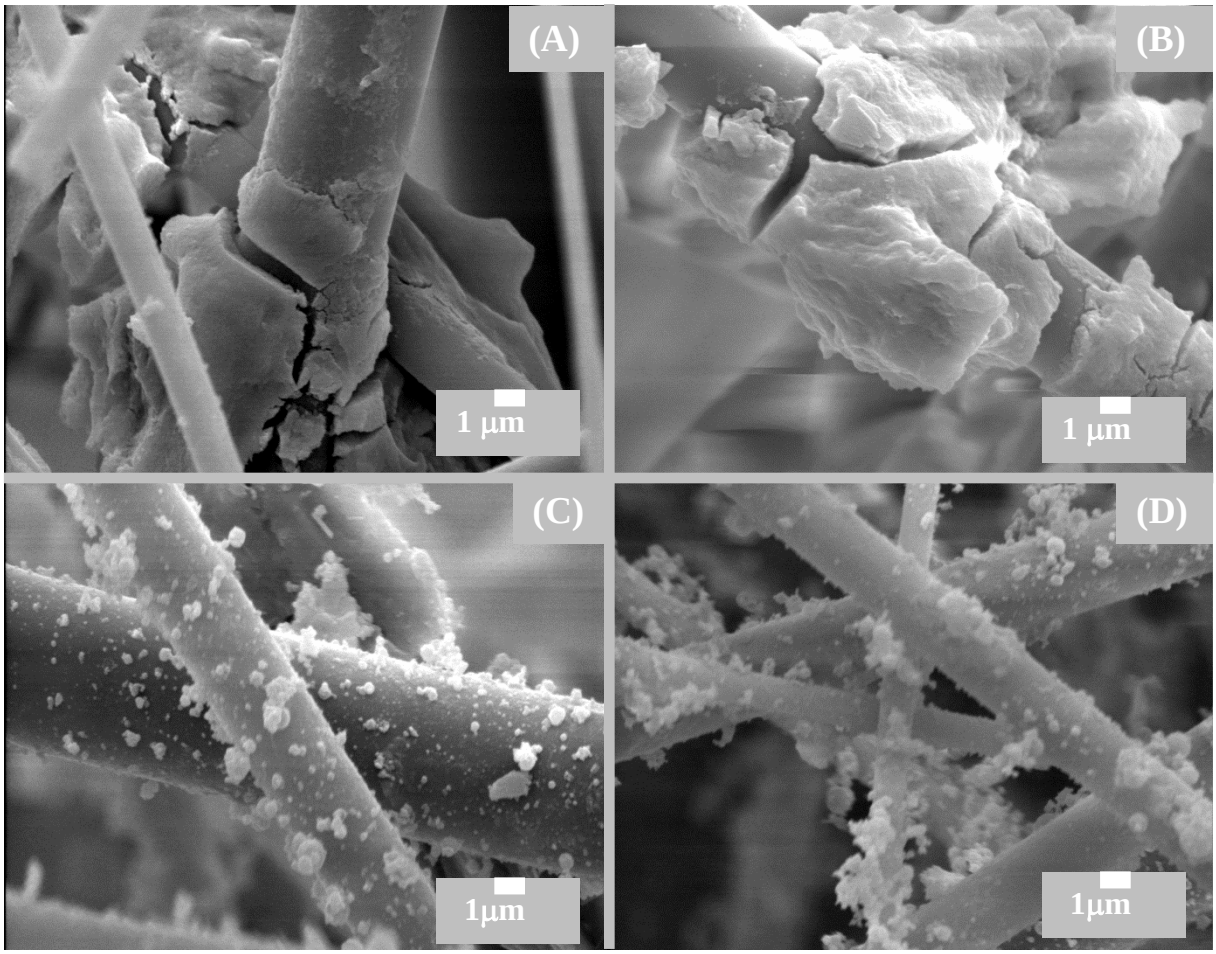


Figure 3. SEM micrographs. Details of catalytic particles, shapes and sizes obtained after drip impregnation or spray deposition on ceramic papers (A) Top face: 10Ce-Ce-Co-600 Imp. (B) Bulk: 10Ce-Ce-Co-600 Imp. (C) Top face: 10Ce-Ce-Co-600 Spray. (D) Bulk: 10Ce-Ce-Co-600 Spray.

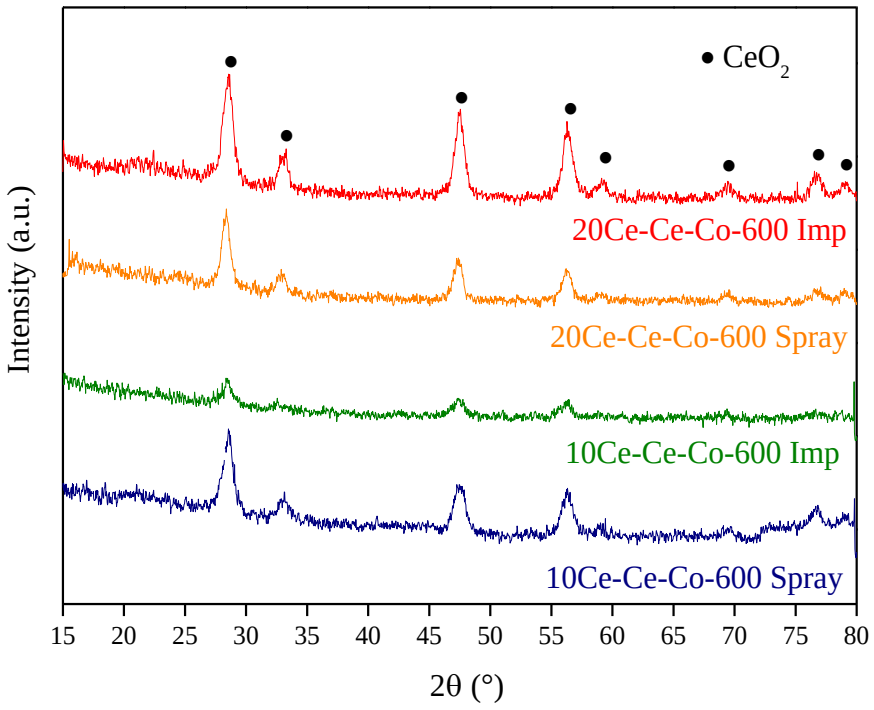


Figure 4. X-Ray diffraction patterns of the catalytic ceramic papers prepared by the spray deposition (Spray) or the drip impregnation (Imp) methods.

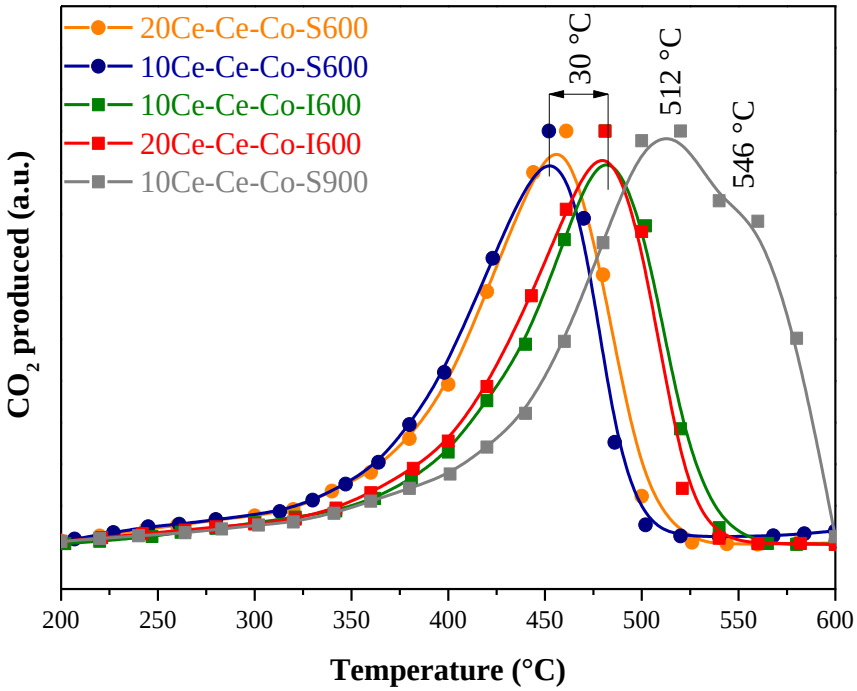
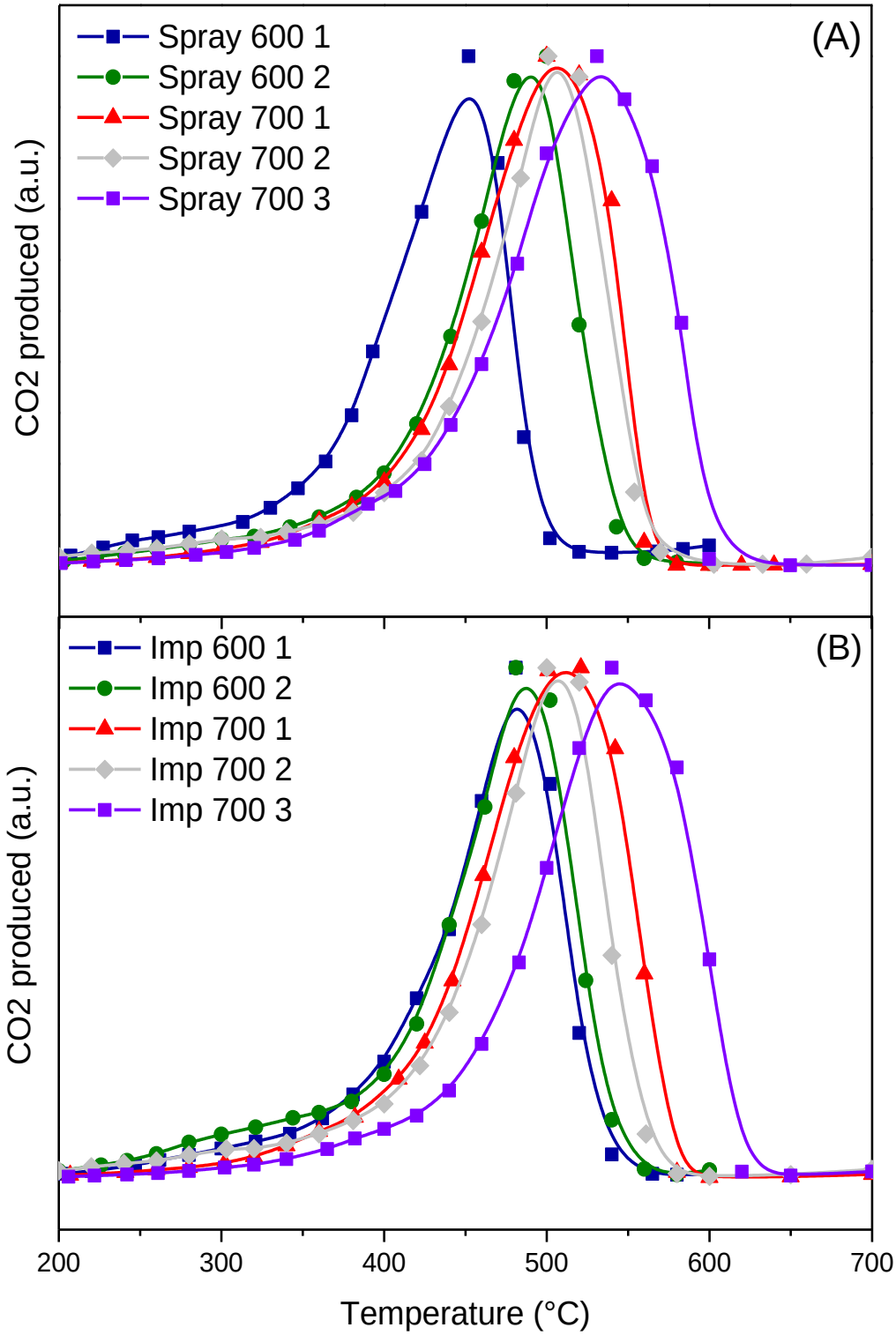


Figure 5. TPO profiles for diesel soot combustion. A 30°C-shift shows the enhancement of the catalytic activity achieved when applying the spray deposition method as compared to the drip impregnation method.

Supplementary information



Stability test: TPO cycles between room temperature and 600 °C (or 700°C) under reaction conditions with a heating rate of 5°C/min (see Experimental for details).
(A) 10Ce-Ce-Co-600-Spray, (B) 10Ce-Ce-Co-600-Imp. Numbers at the end indicate the run order at each temperature (1=first, 2=second and 3=third).